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Xylidine-polluted groundwater purification. Ozonation and catalytic wet oxidation

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Abstract. This paper discusses the removal of xylidines from polluted waters by means of chemical oxidation methods. Xylidines, persistent compounds of rocket fuel, have been detected in high concentrations in groundwater in the areas of former Soviet missile bases. To treat such groundwater, two chemical processes, ozonation and catalytic wet oxidation, were studied. The kinetics of degradation of 2,4-xylidine by ozonation was investigated in a wetted-wall column. A laboratory-scale ozone–water contact column was designed and a steady-state wetted wall reactor model was developed. The ozonation model with the estimated parameters showed good agreement between predicted and experimental data. The estimated reaction rate coefficients could be used for the design of a bubble ozonation column for xylidine-polluted groundwater treatment. The developed model and experimental set-up can be used in the future to estimate the kinetic parameters of ozonation reactions involving other similar compounds. Catalytic wet oxidation was carried out in a stirred batch autoclave in the presence of granulated activated carbon. 2,4-Xylidine was concentrated on the surface of the granulated activated carbon and then oxidized at different temperatures (140–170 °C) and oxygen partial pressures (4–10 atm). The GAC type catalyst was active enough for 2,4-xylidine oxidation, but not for the oxidation of the formed organic acids. Degradation of organic acids needs severer conditions. Both chemical oxidation processes could be used as a pre-treatment before biological treatment. The results of this paper can be used to design two chemical processes for purification of xylidine polluted water.

Key words: 2,4-xylidine, ozonation, wetted wall column, catalytic wet oxidation, mathematical modelling, reaction kinetics.

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INTRODUCTION

Xylidine-polluted groundwater can be found in the sites of former Soviet military missile bases due to spills of a xylidine-based missile fuel – samine. The fuel consists of triethylamine (50 wt%) and xylidines or dimethylanilines (45 wt%) [1]. The precise composition of the rocket fuel can be found in the literature [2]. Similar contamination of groundwater occurs at former military bases in Barta and Tasi, West Latvia [3]. Triethylamine is an easily volatile component and therefore we focused on the treatment of xylidines, the main unvolatile toxic components of samine.

Xylidines are toxic and mutagenic compounds. Typically, xylidines are a mixture of isomers in which the 2,4-, 2,5-, and 2,6-isomers are dominant. Molecular structures of isomers are presented in Fig. 1. They are relatively soluble, mobile, and persistent in groundwater [4]. Based on the effects seen in animals, it is likely that xylidine can be absorbed through skin in sufficient amounts to cause dangerous methemoglobinemia [5]. The maximally allowable concentration of aromatic amines (including xylidines) in drinking groundwater is 0.1 μg/L [6].

Several investigations have been carried out on the purification of water contaminated with aromatic amines, including xylidines. Some of them are presented in our previous study [7].

Among physical wasterwater treatment methods, adsorption on granulated activated carbon (GAC) has been the most common treatment because of its simplicity, effectiveness, and relatively low price. The method is largely used in the purification of groundwater [8, 9] from organic pollutants. Despite the fact that adsorption gives a good purification effect, the pollution is not totally eliminated but only transferred from one medium to another. Rising costs, particularly those associated with the disposal of used GAC, are raising the competitiveness of chemical oxidation methods.

The main target of this study was to investigate the feasibility of the treatment of xylidine-polluted groundwater by means of chemical methods and to develop

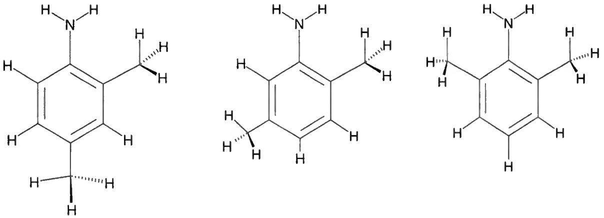

Fig. 1. The molecular structures of 2,4-, 2,5-, and 2,6-dimethylaniline.

a theoretical basis for the design of the treatment processes. To achieve the target, two processes were experimentally studied and mathematically modelled: ozonation and catalytic wet oxidation (CWO) using GAC as a catalyst.

The reaction rate coefficients of 2,4-xylidine ozonation are not available in the literature. In order to design an ozone reactor for 2,4-xylidine destruction on a rational basis, these kinetic parameters must be evaluated from the laboratory experiments.

Another target was to evaluate the reaction kinetics of CWO in the presence of GAC. The CWO process could be used as a regeneration unit in the integrated adsorption process. The pollutant is concentrated on the surface of GAC and then degraded in the wet oxidation unit.

Ozonation

Ozonation is a well-established technology capable of destroying a wide range of organic molecules, including toxic organics. Ozone is a very reactive and powerful oxidizing agent ($E^0 = 2.07$ V) compared to other oxidizing agents, such as chlorine (1.36 V) and H_2O_2 (1.78 V) [10]. A considerable disadvantage of ozone can be high production costs. Moreover, high capital cost of the ozonation unit makes ozonation technologies best suited to large-scale applications [11].

The reaction between ozone and aromatics includes the insertion of oxygen into the benzene ring, which results in the breaking of the double bonds. The opening of the benzene ring usually requires 1–2 moles of ozone per mole of aromatics [12].

Aromatic amines decompose to several by-products during ozonation (e.g., nitrobenzene and azobenzene, acetic and formic acid) [13–15] before mineralization. Most of the reaction products are biodegradable and less toxic than the reactants.

The kinetic parameters for reactions between xylidines and ozone are not available in the literature. In order to design a larger-scale ozone contactor (e.g., a bubble column, stirred tank reactor, etc.) for the treatment of polluted groundwater, the reaction rate coefficients should be known. In the present work, a wetted-wall reactor was used for evaluating the kinetic parameters of the reaction. The wetted-wall reactor provides an advantage in reaction kinetics research because of its precisely known mass transfer area and absence of foaming. However, a wetted-wall reactor can be used for fast reactions only; otherwise the contact time is too short for sufficient concentration changes to be observed. The coefficients of the ozonation reaction rate for aromatic amines show adequate values [16, 17] in order for the above-mentioned reactor system to be used.

A steady-state mathematical model that takes into account the mass transfer between phases, the reaction between ozone and xylidine, xylidine vaporization, the enhancement of the mass transfer due to the reaction between ozone and xylidine, and the stoichiometric ratio of the consumed ozone to the reacted xylidine was developed for the wetted-wall reactor.

The developed model and experimental set-up can be used in the future for the estimation of the kinetic parameters of reactions involving other similar compounds. The estimated rate coefficients could be used for the design of bubble ozonation columns. The values of the volumetric ozone mass-transfer coefficient can be easily obtained from the oxygen mass transfer data [18].

Catalytic wet oxidation

Among the treatments of nitrogen-containing organic compounds in water, wet air oxidation (WAO) appears as one of the most promising [19]. The idea of the wet oxidation process is to enhance contact between molecular oxygen and the organic matter to be oxidized [20]. Nevertheless, in order to obtain high conversions for pollutants, the non-catalytic techniques need severe operating conditions in terms of temperature and pressure. The CWO process with molecular oxygen using GAC at mild conditions (temperature below 200°C, pressure below 15 atm) reduces significantly the severity of the wet oxidation process and constitutes an economically attractive pretreatment step for non-biodegradable aqueous pollution due to its low capital and operating costs [21].

The CWO process can be carried out in a tubular packed-bed reactor operating in the trickle flow regime using air oxygen as an oxidant. In these conditions, chlorinated and nitroaromatic compounds (e.g. phenol) are oxidized over a solid catalyst in a three-phase system under mild conditions of oxygen partial pressure (6–12 atm) and temperature (120–160°C) [22]. The activated carbon has been demonstrated to have catalytic effect on the wet oxidation of phenols. The oxidation can be carried out even in mild conditions of air pressure (4.7 atm) and temperature (40°C) with 48% of phenol conversion [23].

The different steps of the reaction mechanism of the wet oxidation of nitroaromatics involved in the process can be summarized as shown in Fig. 2 [24].

It clearly appears that acetic acid and ammonia are the most refractory compounds. Both oxides and supported noble metals can be used in the CWO of organic compounds. However, catalysts active in steps I and II could be different

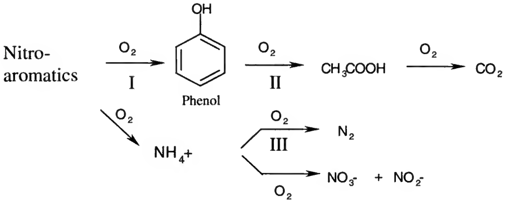

Fig. 2. General pathway of degradation of nitroaromatics by wet oxidation.

from those that are active and selective to N_2 in step III. The end products are very resistant to total oxidation even under severe conditions and their oxidation to carbon dioxide is usually the rate-limiting step [25]. A reaction mechanism similar to the nitroaromatics oxidation scheme (Fig. 2) is supposed to take place in the 2,4-xylidine degradation process; the first step for xylidine oxidation is probably just the formation of nitroaromatics.

EXPERIMENTAL PART

Chemical oxidation methods, such as ozonation and catalytic wet oxidation in the presence of GAC, were studied experimentally. The following chapter gives a brief overview of the experimental part of the study.

All the experiments were carried out on a model solution (2,4-xylidine and distilled water). The 98% pure 2,4-xylidine solution was obtained from MERCK-Schuchardt (Germany).

Ozonation

The ozonation kinetics and mass transfer experiments were carried out on a wetted-wall reactor (Fig. 3). The height of the wetted-wall ozonation column (a glass tube) was 1 m and its inner diameter was 0.015 m. The column was carefully set in a vertical position and was equipped with special sections prior to the gas and liquid inlets and outlets in order to maintain a stable annular flow. The use of the glass tube made it possible to observe the complete wetting of the inner wall.

Ozonation experiments were carried out at room temperature (20°C). The operation mode of the reactor was countercurrent. To achieve a complete film distribution, the reactor was washed with a NaOH solution and rinsed with distilled water before runs. Polluted water was fed into the top of the reactor with the help of a peristaltic pump. Ozone was generated from pressured air by a laboratory ozone generator (*Trailigaz* "Labo 10"). The ozone–air mixture was fed into the system through a fluoroplast pipe from the bottom of the reactor. Sampling was carried out while the system was at a steady state. The liquid phase concentration of the 2,4-xylidine was measured inside the feed tank and at the outlet of the liquid. The ozone concentration was measured at the inlet and outlet of the gas phase. In mass transfer experiments (no reaction), the ozone concentration was measured additionally in a liquid effluent. The volumetric flow rate of the gas feed was measured by a rotameter. The pH was measured for all the samples before and after ozonation. The main values of the experimental parameters as well as experimental results are presented in [26]. The experimentally observed parameters varied in a range presented in Table 1.

It was observed that the pH of the solution decreased during the ozonation (by about 1 unit), indicating that in the degradation process acids are formed. The

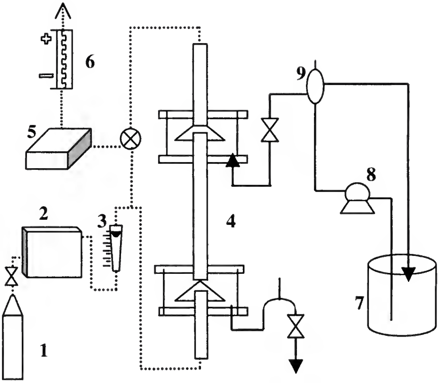

Fig. 3. Schematic diagram of the wetted-wall reactor system. 1 – pressurized air cylinder, 2 – ozone generator, 3 – rotameter, 4 – wetted-wall reactor, 5 – spectrophotometer, 6 – ozone destructor, 7 – feed storage tank, 8 – peristaltic pump, 9 – overflow.

Table 1. Experimentally observed variables

Variable	Notation	Unit	Range
Solution pH	pH	–	3.34–7.52
Liquid residence time	t	s	4.6–12.6
Liquid flow rate	Q_L	L/min	0.04–0.18
Gas flow rate	Q_G	L/min	1.2–2.1
2,4-Xylidine concentration	c^{xyl}_{Lin}, c^{xyl}_{Lout}	mg/L	54–200, 45–182
Ozone concentration	$c^{O_3}_{Lin}$, $c^{O_3}_{Gout}$	mg/L	13.2–22.7, 9.6–20.3
Biodegradability in	BOD_7/COD_{in}	–	0–0.01
Biodegradability out	BOD_7/COD_{out}	–	0.05–0.26

colour of the liquid changed from colourless to slightly yellowish at the outlet. The HPLC analyses showed the appearance and decay of 18 peaks. These peaks present the ring-cleavage and final acidic products, which was confirmed by the biodegradability growth in tests. In addition to oxalic acid, the analysis showed the formation of propionic, formic, and acetic acids during the ozonation.

Catalytic wet oxidation

In the study of CWO the influence of the reaction conditions, viz. temperature and oxygen partial pressure, were evaluated. The CWO experiments were carried out in 0.3 L *Parr Series 4561 Mini Reactor* equipped with *Series 4840 Temperature Controller* (made in the USA). A scheme of the reactor system is presented in Fig. 4. The conditions of the CWO experiments are presented in Table 2.

In the CWO experiments, the commercial Granulated Acicated Carbon GAC NORIT RB 1 (made in The Netherlands) was used in adsorption and as the catalyst. High purity compressed oxygen was used as the oxidant (AGA-Finland).

Before the experiments, the reactor and sampling tube were cleaned with distilled water. The cold reactor was then charged with 100 g of 2,4-xylidine saturated wet GAC and 100 mL of residual liquid solution from adsorption experiments. The adsorption isoterms, xylidine diffusion coefficient in GAC

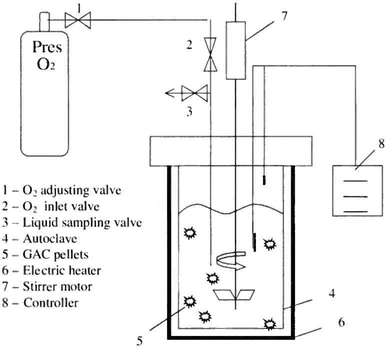
Pres
O_2
1
2
3
4
5
6
7
8
1 – O_2 adjusting valve
2 – O_2 inlet valve
3 – Liquid sampling valve
4 – Autoclave
5 – GAC pellets
6 – Electric heater
7 – Stirrer motor
8 – Controller

Fig. 4. Catalytic wet oxidation reactor system.

Table 2. Experimental conditions of the CWO experiments

Variable	Notation	Unit	Range
Temperature	T	°C	140–170
Total pressure	p^{TOT}	atm	10–15
Oxygen partial pressure	p^{O2}	atm	4–10
2,4-Xylidine concentration	c^{Xyl}	g/L	8–11
GAC concentration	c^{GAC}	$\mathrm{g_{dry}/L}$	265

pores, and breakthrough curves are presented in [7]. The reactor was then sealed and heated to the appropriate test temperature and agitated at 900 rpm stirrer speed. Impeller rotation was set to eliminate any external mass transfer resistance. The thermal equilibrium was achieved in about 1 h after the desired temperature was entered into the temperature controller and the zero sample (5 mL) was taken by opening the liquid sampling valve. Then the oxygen inlet valve was opened and the oxygen pressure was adjusted to a desired level. The stopwatch was immediately started. Samples were taken throughout the run to assess the dependence of the reaction rate on 2,4-xylidine concentration after 10, 30, 60, and 120 min by closing the the O_2-inlet valve and opening the liquid sampling valve. After sampling, the sample valve was closed and the O_2-valve was re-opened, which flushed the sample tube at the same time.

Analysis

The 2,4-xylidine concentration in the liquid phase was determined by a High Performance Liquid Chromatorgaph (Hewlett-Packard HP1100 series with UV and RI detectors) analyser. Analyses used MERCK LiChrosolv® HPLC grade methanol, analytical grade $(NH_4)H_2PO_4$ and $(NH_4)_2HPO_4$, and a 15 cm YMC-Pack Pro C18 column and method from YMC Co, Ltd (Japan). The ozone concentration in the gas phase was measured using a spectrophotometer (*Unicam Helios Beta*) and iodometrically in the liquid phase [27]. The pH of the inlet and outlet liquids was measured using a *Vernier* PH-BTA pH sensor. In addition, the COD was measured with the Hach standard method [28a], using a Portable Datalogging Spectrophotometer Hach DR/2010 at wavelength 605 nm. BOD_7 was measured with a standard method [28b], using a Marvet Junior dissolved oxygen meter.

In CWO the total organic carbon (TOC) content was analysed by Shimadzu Total Organic Carbon Analyzer TOC-5050A.

MODELLING: RESULTS AND DISCUSSION

Ozonation

A steady-state wetted wall reactor model was developed taking into account the mass transfer between the phases (N), the reaction between ozone and 2,4-xylidine (R), the 2,4-xylidine vaporization, as well as the stoichiometric ratio of the consumed ozone to the reacted 2,4-xylidine. The enhancement of the ozone mass transfer, ϕ^{O_3}, due to the reaction between ozone and 2,4-xylidine was calculated in the model using an equation based on the second-order reaction kinetics [29]. The model was based on countercurrently connected and perfectly mixed mass transfer stages (Fig. 5).

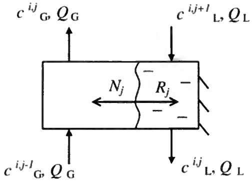

Fig. 5. Modelling block of the *j*th stage of the mass transfer stage. c_L and c_G are the liquid and gas phase concentrations and Q_L and Q_G are the liquid and gas flow rates.

The mass balances for the *i*th ($i = 1$ for ozone and $i = 2$ for 2,4-xylidine) component in the *j*th stage are:

$$Q_L(c_L^{i,j+1} - c_L^{i,j}) + \left[k_L^i a \phi^i \left(\frac{c_G^{i,j}}{H^i} - c_L^j \right) - m^i k c_L^{O_3} c_L^{xyl} \right] F h_L l = 0 \tag{1}$$

for the liquid phase and

$$Q_G(c_G^{i,j-1} - c_G^{i,j}) - k_L^i a \phi^i \left(\frac{c_G^{i,j}}{H^i} - c_L^{i,j} \right) F h_L l = 0 \tag{2}$$

for the gas phase, where F is the cross-sectional area of the reactor, l is the height of the stage ($l = L/n = 0.1$ m, where L is the total length of the reactor and n is the number of stages), H^i is Henry's dimensionless coefficient calculated for ozone according to IOA [30] ($H^{O_3} = 4.12$ at 20°C) and for 2,4-xylidine obtained from the literature ($H^{xyl} = 0.27$ [31]). The stiochiometric coefficient and enhancement factor for 2,4-xylidine are equal to one ($m^{xyl} = 1$ and $\phi^{xyl} = 1$). The mass-transfer coefficient for 2,4-xylidine, k_L^{xyl}, was calculated using the equation based on the penetration mass transfer theory in dilute solutions [32] and for ozone was estimated experimentally (Eq. 6) from the ozone mass-transfer experiments (no reaction).

The liquid hold-up, h_L, is calculated from the following equation:

$$h_L = \frac{\pi d \delta}{F}, \tag{3}$$

where d is the column's inner diameter, F is the cross-sectional area, and the liquid film thickness for the laminar flow, δ, is obtained from the following equation [33]:

$$\delta = \sqrt[3]{\frac{3\mu\Gamma}{g\rho^2}}, \tag{4}$$

where Γ is the liquid mass flow rate per wetted perimeter, μ is the liquid dynamic viscosity, ρ is the liquid density, and g is the gravitational acceleration.

Parameter estimation

The developed mathematical model was coupled with the parameter estimation program [34]. First, the ozone mass-transfer coefficient, $k_{\mathrm{L}}^{\mathrm{O_3}}$, for the wetted wall column was estimated from the pure water–ozone mass-transfer experiments (self-decomposition of ozone was ignored). The objective function was used to minimize the differences between the observed and predicted ozone concentrations as follows:

$$\Phi=\sum_{l=1}^{N}(c_{\mathrm{Lout},l}^{\mathrm{O_3,calc}}-c_{\mathrm{Lout},l}^{\mathrm{O_3,exp}})^2+\sum_{l=1}^{N}(c_{\mathrm{Gout},l}^{\mathrm{O_3,calc}}-c_{\mathrm{Gout},l}^{\mathrm{O_3,exp}})^2, \tag{5}$$

where N is the number of observations.

The dependence of $k_{\mathrm{L}}^{\mathrm{O_3}}$ [m/s] on the liquid flow rate Γ in the laminar-wavy film flow range (0.01–0.09 kg/m s) in the wetted-wall reactor resulted in the following relation with the estimated parameters e and p:

$$k_{\mathrm{L}}^{\mathrm{O_3}}=e\Gamma^{p}=0.443\,10^{-4}\,\Gamma^{0.411}. \tag{6}$$

The reaction rate and the stoichiometric coefficient for ozone ($k^{\mathrm{O_3}}$ and $m^{\mathrm{O_3}}$) were estimated from the experimentally measured concentrations of $c_{\mathrm{Lout}}^{\mathrm{xyl}}$ and $c_{\mathrm{Gout}}^{\mathrm{O_3}}$, obtained from the experiments. The sum of the residual squares

$$\Phi=\sum_{l=1}^{N}(c_{\mathrm{Lout},l}^{\mathrm{xyl,calc}}-c_{\mathrm{Lout},l}^{\mathrm{xyl,exp}})^2+\sum_{l=1}^{N}(c_{\mathrm{Gout},l}^{\mathrm{O_3,calc}}-c_{\mathrm{Gout},l}^{\mathrm{O_3,exp}})^2, \tag{7}$$

was minimized in the estimation. The quality of the data fitting was checked with the degree of explanation, R^2, defined as follows:

$$R^2=1-\frac{\sum_{l=1}^{N}\sum_{i=1}^{2}(c_{l,i}^{\mathrm{exp}}-c_{l,i}^{\mathrm{calc}})^2}{\sum_{l=1}^{N}\sum_{i=1}^{2}(c_{l,i}^{\mathrm{exp}}-c_{l,i}^{\mathrm{mean}})^2}. \tag{8}$$

The estimated parameters, 95% confidence limits, and the degree of explanation, R^2, are presented in Table 3.

The elaborated steady-state wetted-wall ozonation reactor model was able to describe the evolution of the pollutant and ozone concentrations in the liquid and gas phases along the reactor length coordinate in various conditions, as presented in Fig. 6.

The model for the wetted-wall reactor showed a good agreement when validated against experimental data (see Fig. 7).

Table 3. Estimated parameters of 2,4-xylidine ozonation

Parameter	Unit	Value	95% confidence limits		R^2
			Lower	Upper	
e		4.43×10^{-4}	1.61×10^{-5}	7.25×10^{-5}	0.994
p		0.411	0.287	0.429	
k^{O_3}	L/(mol s)	0.316×10^{5}	1.67×10^{3}	4.65×10^{3}	0.961
m^{O_3}	mol/mol	2.45	1.74	3.16	

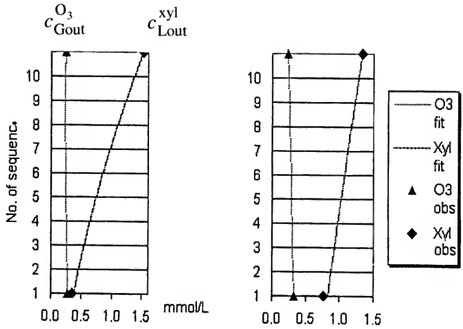

Fig. 6. Concentration profiles of two runs.

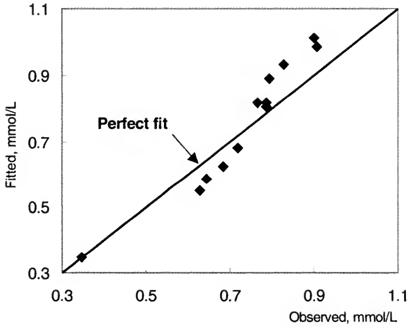

Fig. 7. Calculated versus observed 2,4-xylidine effluent concentration in the liquid phase.

Kinetic models for catalytic wet oxidation

Several completely different sets of kinetic models have been reported for CWO [35]. In this study the reaction was modelled in terms of the Langmuir–Hinshelwood kinetic model and with the power law kinetics (second-order kinetic model). It can be noted that both models predict satisfactory 2,4-xylidine degradation in the CWO process. HPLC analysis showed the formation and decay of several intermediate compounds. The exact concentrations of these species were not measured and the CWO models were developed without intermediates.

Langmuir–Hinshelwood model

The Langmuir–Hinshelwood kinetic model for CWO reaction is theoretically most justified. It assumes an irreversible surface reaction between the absorbed reactants (2,4-xylidine and oxygen). The reaction rate of xylidine is a function of the concentrations of the reacting species on the surface of the GAC. The surface reaction of chemisorbed 2,4-xylidine and oxygen is rate controlling as follows [36]:

$$\frac{dc^{\mathrm{xyl}}}{dt} = -k\frac{K^{\mathrm{xyl}}c^{\mathrm{xyl}}\sqrt{K^{\mathrm{O_2}}c^{\mathrm{O_2}}}}{\left(1+K^{\mathrm{xyl}}c^{\mathrm{xyl}}+\sqrt{K^{\mathrm{O_2}}c^{\mathrm{O_2}}}\right)^2}, \tag{9}$$

where k is the reaction rate coefficient, and K^{xyl} and $K^{\mathrm{O_2}}$ are the adsorption coefficients of 2,4-xylidine and oxygen, respectively.

The temperature dependence of the adsorption coefficient on higher temperatures is presented by the van't Hoff equation as follows:

$$K = K_0 e^{-\frac{\Delta H}{RT}}, \tag{10}$$

where K_0 is the pre-exponential factor and ΔH is the heat of adsorption.

The temperature dependence of the reaction rate coefficient, k, is determined by the Arrhenius equation:

$$k = k_0 e^{-\frac{E_\mathrm{a}}{RT}}, \tag{11}$$

where k_0 is the pre-exponential factor and E_a is the activation energy.

The oxygen concentration in the liquid phase was calculated using the following oxygen solubility equation [37]:

$$c^{\mathrm{O_2}} = p^{\mathrm{O_2}} e^{\frac{0.046T^2+203.357T\ln\left(\frac{T}{298}\right)-(299.378+0.092T)(T-298)-20.591\cdot10^3}{8.3144T}}, \tag{12}$$

where $p^{\mathrm{O_2}}$ is the oxygen partial pressure.

In the optimization routine, the oxygen adsorption coefficient parameters, $K_0^{O_2}$ and ΔH^{O_2}, as well as the pre-exponential factor, k_0, and activation energy, E_a, for the Langmuir–Hinshelwood kinetic model (Eq. 9) were estimated. The values of parameters in the 2,4-xylidine adsorption coefficient (Eq. 10) in the temperature range of 415–450 K were separately estimated from the mass balances at the end of the pre-heating period before oxygen was added.

Power-rate law model

The simplest rate equation that would adequately fit the experimental data is the power-rate law model. The reaction kinetics is presented formally through a direct oxidation reaction in the liquid phase, including oxygen and 2,4-xylidine concentrations in the liquid phase. The rate of reaction is given by [38]:

$$\frac{dc_{\mathrm{xyl}}}{dt} = -k(c^{\mathrm{xyl}})^x (c^{O_2})^y, \tag{13}$$

where k is the reaction rate constant, c^{xyl} and c^{O_2} are the concentrations of 2,4-xylidine and dissolved oxygen in the liquid phase, and superscripts x and y are reaction orders.

This model is entirely empirical, and it does not take into account the adsorption on the catalyst surface in the heterogeneous CWO, which are included in Eq. 9. The equation is correct for the wet oxidation without catalyst. In the parameter estimation routine, the pre-exponential factor, k_0, activation energy, E_a, and reaction orders x and y were estimated.

Parameter estimation

The two models were implemented so that it was easy to link the model into the optimization algorithm of the *Flowbat* program framework [34]. The Davidson optimization routine was used for parameter estimation. All the parameters except K_0^{xyl} and ΔH^{xyl} were evaluated simultaneously.

On the basis of the 2,4-xylidine decay, the apparent activation energies and pre-exponential constants were determined for the reactions of the CWO and the WAO, with and without catalyst, using a parameter estimation program. The objective function was

$$\Phi = \sum_{l=1}^{N} (c_l^{\mathrm{xyl,calc}} - c_l^{\mathrm{xyl,exp}})^2, \tag{14}$$

where N is the total number of observations.

The results of the parameter estimation of the power-rate law and Langmuir–Hinshelwood kinetic model kinetics are presented in Tables 4 and 5.

Table 4. Estimated parameters for catalytic wet oxidation

Parameter	Unit	Value	Model
			Langmuir–Hinshelwood, Eq. 9
k_0	mol/min	5.72×10^3	Eq. 11
E_a	kJ/mol	31.3	Eq. 11
$K_0^{O_2}$	m^3/mol	8.8×10^{-3}	Eq. 10
ΔH^{O_2}	kJ/mol	−13.2	Eq. 10
K_0^{xyl}	m^3/mol	3.45×10^{-3}	Eq. 10
ΔH^{xyl}	kJ/mol	−18.1	Eq. 10
			Power-rate model, Eq. 13
k_0	mol/min	80.3	Eq. 11
E_a	kJ/mol	5.59	Eq. 11
x	–	1.01	Eq. 13
y	–	1.00	Eq. 13

Table 5. Estimated parameters for wet air oxidation (experiments without catalyst)

Parameter	Unit	Value	Model
			Power-rate model, Eq. 13
k_0	1/min	1.18	Eq. 11
E_a	kJ/mol	20.3	Eq. 11

As can be seen from Table 4, the reaction between 2,4-xylidine and oxygen is formally a typical second-order reaction, first-order in respect to both reactants. In WAO experiments, the oxygen partial pressure was kept constant and the oxidation reaction was first-order in respect to 2,4-xylidine.

A satisfactory fit was achieved with both the CWO models when validated against experimental data. The effect of temperature on the 2,4-xylidine degradation under constant oxygen pressure, $p^{O_2} = 5$ atm, is presented in Fig. 8 and the effect of oxygen partial pressure under constant temperature, $T = 430$ K, is presented in Fig. 9. Predictions for the WAO without catalyst in Fig. 8 were calculated from the power-law kinetic model (Eq. 13) and for the CWO, from the Langmuir–Hinshelwood kinetic model (Eq. 9). Predictions for the CWO by the power-law are presented in [39].

Catalytic wet oxidation under operating conditions completely oxidized 2,4-xylidine. The TOC degradation was significant but not 100% complete. The TOC reduction was incomplete because the 2,4-xylidine degradation pathway involves side reactions that lead to the formation of stable acids. The HPLC analysis indicated that over 20 intermediates were formed. Some of the organic compounds, such as propionic and formic acids, were determined throughout the analysis.

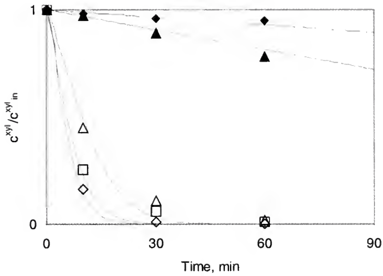

Fig. 8. Measured normalized 2,4-xylidine concentration plotted versus reaction time for three temperatures (◇ – 450 K, □ – 430 K, and △ – 415 K) at p_{O2} = 5 atm. Symbols denote experimental data and lines denote prediction from the kinetic model. Filled symbols denote experiments without GAC for two temperatures (◆ – 415 K and ▲ – 450 K) with predictions with lines.

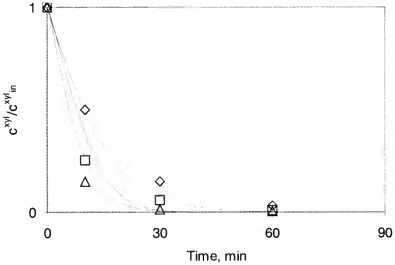

Fig. 9. Measured normalized 2,4-xylidine concentration plotted versus reaction time for three oxygen partial pressures (△ – 4 atm, □ – 5 atm, and ◇ – 10 atm) at 430 K. Symbols denote experimental data and lines denote prediction from the kinetic model.

COMPARISON OF TREATMENT METHODS

Ozonation gives a good effect in destructing xylidines but complete mineralization is not feasible. The same concerns the CWO process because organic acids, which are formed throughout the oxidation process, are resistant to wet oxidation. In addition the ozonation process is feasible for large-scale applications whilst adsorption onto GAC with subsequent CWO can be economically used for small-scale purification plants.

Before CWO, the pollutant is adsorbed on the surface of GAC as the first step (see breaktrough curves in [7]). In the second step of CWO, the 2,4-xylidine is oxidized in the presence of dissolved oxygen and the GAC acts as a catalyst. In our experiments, the 2,4-xylidine was almost completely oxidized in the CWO reactor within an hour at relatively mild temperatures (140–175 °C) and oxygen partial pressures (4–10 atm). Non-catalytic wet oxidation was not so effective for 2,4-xylidine removal.

It must still be born in mind that in the study a model solution was used in laboratory experiments and the kinetic parameters were estimated for the xylidines–distilled water system and therefore before real groundwater purification additional laboratory experiments must be carried out with *in situ* water, taking into account the deviations due to the water quality (additional organics, pH, etc.).

CONCLUSIONS

Xylidines are carcinogenic compounds originating from missile fuel and are dominating in polluted groundwater in the areas of abandoned Soviet missile bases in Eastern Europe. Two chemical methods for xylidine-polluted water purification were studied – ozonation and catalytic wet oxidation.

Ozonation of 2,4-xylidine in aqueous solution was carried out on a wetted-wall column. A laboratory-scale ozone contactor was designed and a steady-state wetted-wall reactor model was developed. The model was based on counter-currently connected and perfectly mixed mass transfer stages. It was possible to describe the changes of the pollutant and ozone concentrations along the reactor length coordinate in various conditions. The mathematical model elaborated for the wetted-wall reactor was observed to be in good agreement with the experimental data – the degree of explanation exceeded 96% for both the ozone mass transfer and the 2,4-xylidine ozonation data.

The developed wetted-wall reactor model is suitable for the investigation of ozonation kinetics for other organic compounds with similar nature. It is easy to include the intermediates into the reaction scheme, as the equation system for each stage of the ozonation column is solved numerically.

The catalytic wet oxidation with GAC as a catalyst at mild conditions (temperature below 200 °C, total pressure below 15 bar) was experimentally studied. The 2,4-xylidine was adsorbed on the surface of the GAC and then degraded in the wet oxidation unit. The GAC type catalyst is active enough for 2,4-xylidine oxidation. The 2,4-xylidine was almost completely oxidized in the CWO reactor within an hour, while the intermediates such as ring cleavage by-products and organic acids, which are formed throughout the oxidation process, are resistant to degradation. The non-catalytic wet oxidation did not degrade 2,4-xylidine at mild conditions and needs severer conditions.

Two kinetic models for predicting 2,4-xylidine degradation in the catalytic wet oxidation were studied. The Langmuir–Hinshelwood and the power-rate law kinetic models were both based on 2,4-xylidine decay. A satisfactory fit was achieved with both when validated against experimental data. The Langmuir–Hinshelwood kinetic model should be used in the reactor design as it has solid theoretical foundation.

In order to obtain more exact results, for the modelling of 2,4-xylidine degradation advanced CWO kinetic models that take into account the formation of intermediate products and their adsorption and desorption should be used. These intermediate products should be identified and quantitatively measured during the experiment. In this study only some of these intermediates were analytically identified (formic, acidic, and propionic acids).

Despite the formation of refractory compounds, the oxidation processes increase the biodegradability of the aqueous solution, since these intermediate products and organic acids are more biodegradable than 2,4-xylidine. A combination of chemical oxidation (ozonation, CWO) and biological treatment could be successfully used.

This study gives a mathematical tool and rate coefficients for designing two chemical methods for xylidine-polluted groundwater purification: ozonation in a bubble column and adsorption onto GAC NORIT RB1 in a packed bed reactor with a subsequent catalytic wet oxidation in the presence of GAC. The results and models developed can be used to design a purification process when only one contaminant is present. The same approach can also be used for real water containing many compounds if they are presented through one lumped parameter, such as COD, BOD, TOC, etc.

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Ksülidiiniga reostatud põhjavee puhastamine. Osoneerimine ja katalüütiline märghapendus

Janek Reinik ja Juha Kallas

On uuritud kantserogeense ksülidiiniga reostatud vee puhastamist osoneerimise ja katalüütilise märghapenduse meetoditega. Niimoodi saastunud põhjavett leidub endistes Nõukogude armee raketibaasides. Ksülidiini lagundamise kineetikat uuriti osoneerimisel läbivoolu kelmereaktoris ja koostati matemaatiline mudel. Mudeliga hinnati reaktsiooni ja massiülekande kiirust. Hinnatud kineetiliste parameetrite alusel arvutatud reaktorist väljuvad kontsentratsioonid sobisid hästi katseliselt määratutega. Antud katseseadet ja mudelit saab kasutada teiste samalaadsete ainete osoneerimise kineetika uurimiseks. Ksülidiini osoneerimise kiiruskonstante on võimalik kasutada barbotaažkolonni projekteerimisel. Keemilistest puhastusmeetoditest uuriti aktiivsöe pinnale kontsentreeritud ksülidiini oksüdeerimist vees hapniku juuresolekul – katalüütiline märghapendus – erinevatel temperatuuridel (140–170°C) ja hapniku osarõhkudel (4–10 atm) perioodilises reaktoris. Aktiivsüsi katalüüsis protsessi ja sellest piisas 2,4-ksülidiini lagundamiseks, kuid ei olnud efektiivne tekkivate orgaaniliste hapete oksüdeerimiseks. Protsessi kasutamine küllastunud granuleeritud aktiivsöe täielikuks regenereerimiseks nõuab karmimaid tingimusi. Märghapenduse modelleerimiseks töötati välja reaktsiooni kineetikat kirjeldavad mudelid.

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Kinetics of $[^3H]$WAY100635 binding to 5-HT$_{1A}$ receptors in rat hippocampal membranes

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Abstract. The binding of $[^3H]$-N-[2-[4-(2-methoxyphenyl)-1-piperazinyl]ethyl]-N-(2-pyridinyl)-cyclohexanecarboxamide ($[^3H]$WAY100635) to 5-HT$_{1A}$ receptors in rat hippocampal membranes was studied. Saturation experiments showed that $[^3H]$WAY100635 binds to a single class of binding sites with very high affinity ($K_D = 87 \pm 4$ pM, $B_{max} = 15.1 \pm 0.2$ fmol/mg protein). The binding of $[^3H]$WAY100635 was reversible, but slow. The dissociation of $[^3H]$WAY100635 from its complex with 5-HT$_{1A}$ receptors was characterized with the $k_{off} = (7.8 \pm 1.1) \times 10^{-3}$ min^{-1}, which means that at low concentrations of the radioligand equilibrium cannot be achieved before 7 h incubation at 25 °C. The obtained data indicate that $[^3H]$WAY100635 is a valuable tool for the determination of the number of 5-HT$_{1A}$ receptor binding sites, but the determination of its affinity is complicated as it hardly reaches equilibrium at concentrations close to its K_D.

Key words: $[^3H]$WAY100635, 5-HT$_{1A}$ receptor, equilibrium, kinetics, affinity, rat hippocampus.

INTRODUCTION

The 5-HT$_{1A}$ (serotonin$_{1A}$) receptor is a member of the family of serotonin (5-HT) receptors, which belong to the superfamily of seven-transmembrane spanning G protein-coupled receptors [1]. The 5-HT$_{1A}$ receptor system has been implicated in a variety of physiological functions and behaviours, including the mood (anxiety and depression) [2], learning, memory, sexual behaviour, and feeding [3]. Therefore the 5-HT$_{1A}$ receptors have become important targets for various psychotherapeutic drugs and an attractive object in screenings for highly selective ligands. For a long time the tritiated derivative of 8-hydroxy-2-(*n*-dipropylamino)tetraline ($[^3H]$-8-OH-DPAT) [4] was the only commercially available specific radioligand for the characterization of 5-HT$_{1A}$ receptors. Over the last years some new radioactive antagonists have been proposed: [^{3}H]-(*R*)-3-*N*, *N*-dicyclobutylamino-8-fluoro-3, 4-dihydro-2*H*-1-benzopyran-5-carboxamide hydrogen (2*R*, 3*R*) tartrate monohydrate ([^{3}H]NAD-299 [5]), and [^{3}H]-N-[2-[4-(2-methoxyphenyl)-1-piperazinyl]ethyl]-N-(2-pyridinyl)-cyclohexane-carboxamide ([^{3}H]WAY100635 [6]). By now, [^{3}H]WAY100635 has become commercially available and has been found to be a useful tool for pharmacological experiments in membrane preparations [7] as well as in brain sections [8]. However, only limited information is available about the kinetic aspects of the binding of [^{3}H]WAY100635 to 5-HT$_{1A}$ receptors [6, 9]. In the present study we used a kinetic approach for characterizing the interactions of [^{3}H]WAY100635 with the 5-HT$_{1A}$ receptors in rat hippocampal membranes. The results indicate that [^{3}H]WAY100635 is a valuable tool for the determination of the number of 5-HT$_{1A}$ receptor binding sites, but the very slow binding seriously complicates the correct determination of the binding affinity of the radioligand.

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METHODS

Hippocampi from Wistar rats were homogenized in 30 vol (ww/v) of 50 mM Tris-HCl buffer (pH 7.4) by Bandelin Sonoplus sonificator (2 passes, both 10 s), incubated for 30 min at room temperature and centrifuged at 43 000 *g* for 20 min at 4 °C. The membrane pellet was washed by re-suspending in 50 mM Tris-HCl buffer and centrifugation was repeated twice. The final pellet was re-suspended in 30 vol (ww/v) of the buffer and stored at −80 °C until use.

In saturation binding experiments the suspension of hippocampal membranes (100 μg/mL) in the incubation buffer containing 50 mM Tris-HCl (pH 7.4) and 0.1 mg/mL bovine serum albumine (BSA) was incubated with different concentrations (0.009–0.75 nM) of [^{3}H]WAY100635 (81 Ci/mmol; Amersham Pharmacia Biotech UK Limited) at 25 °C for an appropriate time. The reaction was terminated and bound radioactivity was separated from free by rapid filtration through a Whatman GF/B glass microfibre filter by washing 3 times with 3 mL of 20 mM K-phosphate-buffer (pH 7.4) containing 100 mM NaCl. The radioactivity content of the filters was counted in 5 mL of scintillation cocktail OptiPhase HiSafe®3 (Wallac Perkin Elmer Life Sciences) by Beckman LS 1800 scintillation counter [10]. The specific binding was determined as the difference between total and non-specific binding, measured in the absence and presence of 10 μM (S)-N-tert-butyl-3-(4-(2-methoxyphenyl)-piperazin-1-yl)-2-phenylpropanamide dihydrochloride (WAY100135) or 8-OH-DPAT, respectively. Displacement studies were performed the same way, including 0.5–0.9 nM [^{3}H]WAY100635 and appropriate concentrations of non-labelled ligands.

Association kinetic experiments were started with the addition of [^{3}H]WAY100635 (final concentration 0.08–4.5 nM) to a membrane suspension in the incubation buffer. At timed intervals aliquots (200–1000 μl depending on the radioligand concentration) were taken and filtered on GF/B as described above. Parallel incubations with the same concentration of [^{3}H]WAY100635 and 10 μM 5-HT or WAY100135 were used to estimate non-specific binding.

Dissociation kinetics was measured after preincubation of membranes with 0.5 nM [^{3}H]WAY100635 for 60 min at 25 °C. Dissociation was then initiated by addition of non-labelled 5-HT (28 μM final concentration) and at timed intervals aliquots (200 μL) were filtered on GF/B and the bound radioactivity was determined as described above.

All data were analysed by means of the non-linear least squares regression method as described in [11] using a commercial program GraphPad PRISM^{TM} (GraphPad, San Diego, CA, USA). Data are presented as mean ± SEM of at least two independent determinations carried out in duplicates. The statistical significance of differences was determined by the Student–Newman–Keuls test, where $P < 0.05$ was taken as the criterion of significance.

RESULTS AND DISCUSSION

The kinetic curves of [^{3}H]WAY100635 binding to rat hippocampal membranes were measured under the excess of radioligand over the receptor concentration. The association of [^{3}H]WAY100635 was well described by the exponential function for the first-order reactions and the observed rate constants (k_{obs}) were obtained at different radioligand concentrations as described earlier [11]. At 0.48 nM of the radioligand the steady-state was achieved within 40 min ($\tau_{1/2} = 7.1 \pm 0.3$ min, Fig. 1), and no additional binding was found during the prolonged incubation time of up to 120 min. Increasing the concentration of the radioligand caused a proportional increase in the association rate, which reached the half life of $\tau_{1/2} = 2.2 \pm 0.2$ min at 3.0 nM of [^{3}H]WAY100635 (Fig. 1, open circles). The analysis of the dependence of the observed association rate constants on the radioligand concentration according to a simple bimolecular reversible ligand binding model revealed the second order rate constant $k_1 = 0.16 \pm 0.02$ nM^{-1} min^{-1}.

The dissociation of [^{3}H]WAY100635 from its complex with 5-HT$_{1A}$ receptors in hippocampal membranes was complete and the equation of the one phase exponential decay revealed a rate constant $k_{off} = (7.8 \pm 1.1) \times 10^{-3}$ min^{-1}, which corresponds to the half time of the dissociation $\tau_{1/2} = 89 \pm 11$ min (Fig. 2). The monophasic exponential decay model was preferred by the F-test in comparison with the two phase exponential decay ($P > 0.05$) in analysis of the dissociation data. The obtained k_{off} value in these experiments agrees with the $k_{-1} = (11 \pm 6) \times 10^{-3}$ min^{-1} calculated from the intercept of the k_{obs} versus [A] plot. The obtained data indicate that the complete dissociation of the radioligand was achieved after at least 7.5 h incubation.

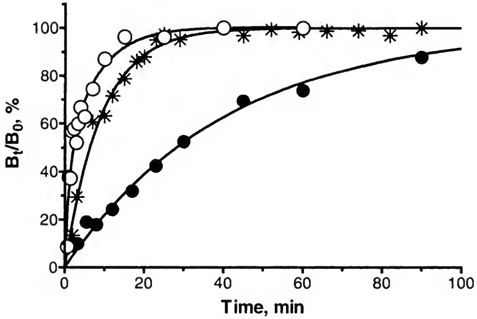

Fig. 1. Time course of specific binding of [^{3}H]WAY100635 to rat hippocampal membranes. The receptor preparations were incubated with 0.07 nM (●), 0.48 nM (∗), or 3.0 nM (○) [^{3}H]WAY100635, and at timed intervals the specifically bound radioactivity in aliquots was determined as described in Methods. The data are presented as the percentage of maximal specific binding at the respective radioligand concentration.

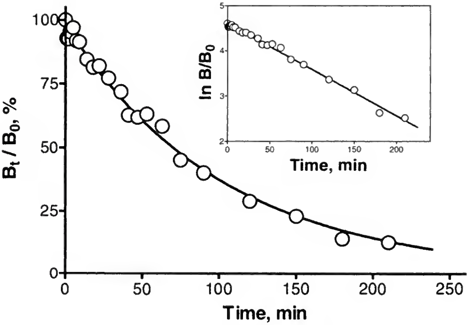

Fig. 2. Dissociation of [^{3}H]WAY100635 from the complex with 5-HT$_{1A}$ receptors in rat hippocampal membranes. The complex was formed by incubation of membranes with 0.5 nM [^{3}H]WAY100635 for 60 min at 25 °C. Dissociation was initiated by addition of large excess (28 μM) of 5-HT. Data are presented as the percentage of the maximal specific binding. **Inset:** Data in semilogarithmic coordinates.

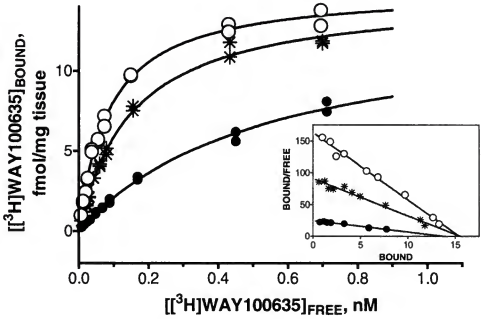

Fig. 3. Specific binding of [^{3}H]WAY100635 to rat hippocampal membranes. The membranes in the incubation buffer (50 mM Tris-HCl (pH 7.4) and 0.1 mg/mL BSA) were incubated with different concentrations of [^{3}H]WAY100635 in the absence (total binding) and presence (nonspecific binding) of 10 μM WAY100135 for 15 min (●), 60 min (✳), or 240 min (○) at 25 °C. The specific binding was defined as the difference between the total and the nonspecific binding. **Inset:** Scatchard plot of the corresponding data.

In the saturation binding experiments the binding of [^{3}H]WAY100635 to rat hippocampal membranes was specific and saturable, and it was characterized with the affinity $K_D = 87 \pm 4$ pM and with the number of the specific binding sites $B_{max} = 15.1 \pm 0.2$ fmol/mg protein (Fig. 3, open circles). The Scatchard plot of these data revealed a straight line and the single-site binding model was preferred also by the F-test in comparison with the two binding site receptor model ($P < 0.05$; Fig. 3, inset). The obtained affinity constant was in general agreement with the constant $K_D = k_{-1}/k_1 = 69$ pM, calculated from the rate constants of the simple reversible reaction. The binding studies with [^{3}H]WAY100635 were carried out in the incubation buffer containing 50 mM Tris-HCl (pH 7.4) and 0.1 mg/mL BSA, which was found to be optimal for the high-affinity binding of the radioligand. The presence of at least 3 mM of Mg^{2+} is usually required for effective coupling of heptahelix receptors with G proteins [12, 13], but for the [^{3}H]WAY100635 binding $MgCl_2$ had a concentration dependent inhibitory effect. Thus, in the presence of 5 mM Mg^{2+} the binding was characterized with the affinity $K_D = 85 \pm 8$ pM and the number of the specific binding sites $B_{max} = 11.1 \pm 0.3$ fmol/mg protein (74% of the control).

Kinetic data indicate that at least 7 h incubation is required to achieve equilibrium at all [^{3}H]WAY100635 concentrations. Shorter incubation times reveal steady-state binding only at higher radioligand concentrations and allowed correct estimation of the number of specific binding sites, but led to underestimation of the binding affinity. Thus, incubation of the reaction medium for

15 min gave $K_D = 540 \pm 50$ pM, while after 60 min incubation the affinity $K_D = 150 \pm 10$ pM and after 240 min, $K_D = 87 \pm 4$ pM (Fig. 3). Slow kinetics of the [^{3}H]WAY100635 binding might explain the large discrepancy between the previously determined dissociation constants (56 pM [9] and 400 pM [14]). However, it is quite complicated to overcome the problem of slow kinetics in experiments with [^{3}H]WAY100635, as we here meet the limits of the method of radioligand binding. First, very high affinity of that radioligand complicates maintenance of the pseudo-first-order reaction conditions ([R]<<[L]) at low concentrations. The reaction will start following the regularities of the second order reaction kinetics, where in addition to the decrease of the receptor concentration also the decrease of the free radioligand concentration during the reaction must be taken into account. Secondly, the receptors have to remain intact during the incubation time. The hippocampal membranes used in our experiments were quite stable loosing the [^{3}H]WAY100635 binding ability with a half life of 27 h (data not shown), which means that within 7.5 h incubation no more than 14% of the binding sites were lost. Such high stability of antagonist binding properties has been also found for other heptahelix G-protein-coupled receptors [11, 15]. In contrast, the high-affinity agonist binding is much more labile [16, 17] and it is shown that in rat hippocampal membranes the half-life of disappearance of binding sites of [^{3}H]-8-OH-DPAT at 25°C is 29 min [16], indicating that an essential part of the high-affinity agonist binding sites may be lost in our experiments as the displacement experiments were carried out with the incubation period of 120 min.

We found that all studied serotonergic ligands were able to displace [^{3}H]WAY100635 binding in concentration-dependent manner and with affinities that were generally in agreement with data reported earlier for 5-HT$_{1A}$ receptors [14, 18–20] (Table 1). Here we saw that Mg^{2+} is required for high-affinity agonist binding and activation of G proteins since 30 μM guanosine-5'–O–(γ-thio) triphosphate (GTPγS) turned the receptors into low-affinity state (Table 1). A slight influence of GTPγS in the presence of Mg^{2+} was also found in the displacement curves of antagonists WAY100135 and 1-(2-methoxyphenyl)-4-(4-[2-phtalimido]butyl)-piperazine (NAN-190), which indicates that binding sites of these ligands are affected by the coupling of G protein and they possess some partial agonist properties as it was proposed also earlier [21, 22]. The good agreement of the obtained data with previously reported data indicates that the use of [^{3}H]WAY100635 seems to be very reasonable for the estimation of affinities of various compounds in the displacement experiments. However, it must be kept in mind that if the binding rate of the competitive ligand is comparable with the [^{3}H]WAY100635 binding, overshot of the radioligand will take place, which may lead to an underestimation of the competitor's affinity [23].

Table 1. The influence of Mg^{2+} and GTPγS on the affinities of serotonergic ligands in the displacement of [^{3}H]WAY100635 in rat hippocampal membranes

Ligand	Control		+30 μM GTPγS	
	K_i^{HIGH}, K_i^{LOW}, nM	α_{HIGH}	K_i^{HIGH}, K_i^{LOW}, nM	α_{HIGH}
5-HT				
EDTA	10±2 780±180	0.40±0.03	758±219	–
5 mM Mg^{2+}	2.1±0.4 110±42	0.63±0.04	525±136	–
8-OH-DPAT				
EDTA	2.1±0.7 35±23	0.67±0.11	15±1	–
5 mM Mg^{2+}	0.21±0.03 22±12	0.78±0.03	0.2±0.1 22±3	0.22±0.03
WAY100135				
EDTA	3.9±0.4	–	4.3±0.3	–
5 mM Mg^{2+}	2.5±0.2	–	4.6±0.3	–
NAN-190				
EDTA	6.8±1.0	–	7.9±1.4	–
5 mM Mg^{2+}	2.5±0.2	–	6.7±1.0	–

High- (K_i^{HIGH}) and low- (K_i^{LOW}) affinity binding constants were calculated from displacement curves against 0.8 nM [^{3}H]WAY100635 using the equations of Cheng–Prusoff [24]. α_{HIGH} indicates the proportion of high affinity binding sites.

– No heterogeneity was detected. The single-site binding model was preferred ($P < 0.05$).

In summary, kinetic analysis gave evidence that the [^{3}H]WAY100635 interaction with 5-HT_{1A} receptors is a specific, slow, and reversible process. Its very high affinity and slow dissociation rate make it a very valuable tool for the determination of the number of 5-HT_{1A} receptor binding sites, and allows its application as a reporter ligand in competition experiments. However, correct determination of the affinity of [^{3}H]WAY100635 is complicated, as due to its slow binding rate and high affinity it hardly reaches equilibrium at concentrations close to its K_D. Therefore, the application of [^{3}H]WAY100635 for assays of 5-HT_{1A} receptor binding properties has several limitations, which should be taken into consideration when planning experiments with this radioligand and when interpreting the obtained data.

ACKNOWLEDGEMENT

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[^{3}H]WAY100635 sidumise kineetika serotoniin 1A retseptoritele roti hipokampuse membraanidel

Sven Parkel ja Ago Rinken

Serotoniini 1A retseptorite spetsiifilise radioligandi [^{3}H]WAY100635 kineetika uurimine roti aju hipokampuse membraanidel näitas, et selle ligandi seostumine 5-HT_{1A} retseptoriga on spetsiifiline, aeglane ja pöörduv protsess. Väga kõrge afiinsuse ja aeglase dissotsiatsiooni tõttu on [^{3}H]WAY100635 suurepärane vahend 5-HT_{1A} retseptorite sidumiskohtade kontsentratsiooni määramiseks ning kasutatav konkureeriva sidumise katsetes teiste ligandide afiinsuste uurimisel. Samas on [^{3}H]WAY100635 afiinsuse määramine problemaatiline, sest aeglase sidumiskiiruse tõttu pole tõeline tasakaal radioligandi K_D-lähedastel kontsentratsioonidel praktiliselt saavutatav.

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Gottfried Wilhelm Osann and ruthenium

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Abstract. Gottfried Wilhelm Osann (1797, Weimar – 1866, Würzburg) was chemistry professor at Tartu University (Universitas Dorpatensis) in 1823–1828. In that period he analysed the crude platinum received from the Ural Mountains and discovered a new platinum metal. He named this metal ruthenium after the medieval name of Russia in Latin. As the quantity of the new element he had was small he could not isolate the metal. This was done several years later and published in 1844 by Carl Claus in Kazan, Russia. Claus is often mentioned as the discoverer of ruthenium and G. W. Osann is forgotten.

Key words: G. W. Osann, ruthenium, discovery of chemical element.

At the turn of the 18th and 19th centuries platinum ores were found in many places of the world and the interest of chemists in their exploitation was great. Many if not most well-known chemists started to analyse the ores and soon four new elements very similar to platinum were discovered. In 1803–1804 Smithson Tennant (1761–1851) discovered osmium and iridium, and William Hyde Wollaston (1766–1828) found rhodium and palladium. The great chemical and physical similarity of platinum metals makes the separation of pure elements from platinum ore an extremely complicated process. For that reason some decades passed before the sixth and last platinum metal was discovered. Gottfried Wilhelm Osann, chemistry professor of Universitas Dorpatensis[1], took successfully part in that research.

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[1] Now the University of Tartu, Estonia. In the 19th century it was a Baltic German university in the Russian Empire.

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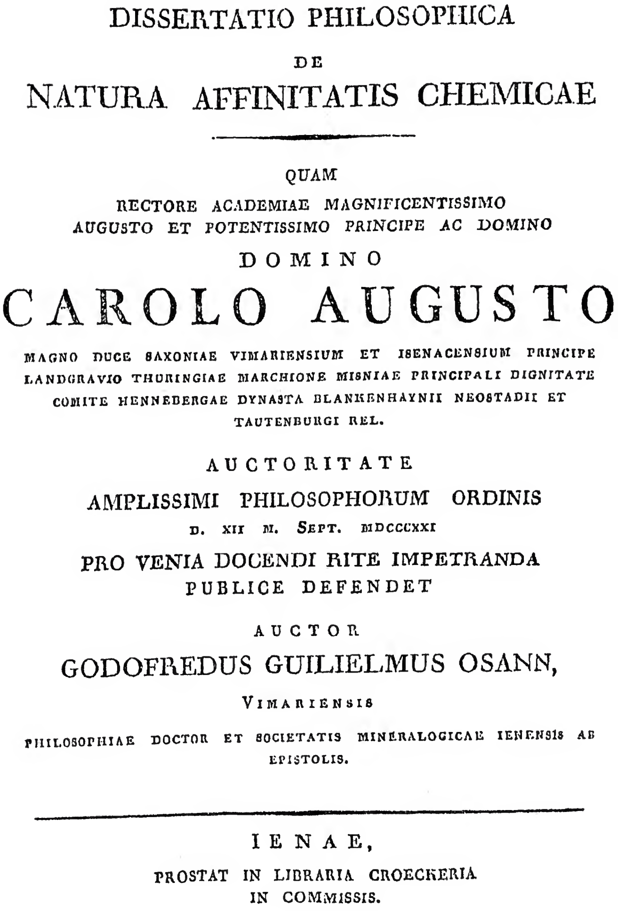

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GODOFREDUS GUILIELMUS OSANN,
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Fig. 1. Title page of the dissertation of Gottfried Wilhelm Osann, Jena, 1821. Bayerische Staatsbibliothek, Id.n.00070370974.

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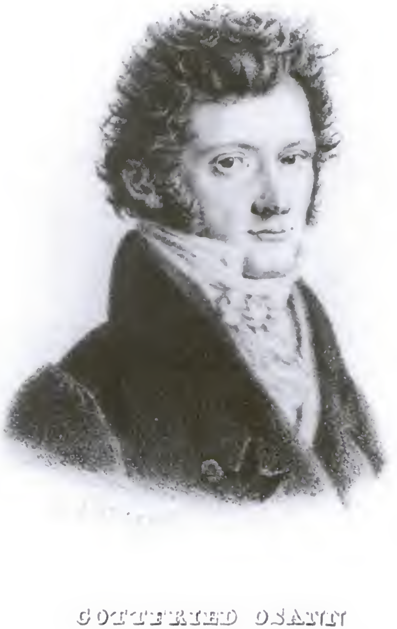

Fig. 2. Doctor and ordinary professor of chemistry Gottfried Osann, 1825. Initials of the author of the lithography: C.v.U.S. EAA, f 402, n 3, s 1237, 1. The author is Carl (Johann Karl Emanuel) von Ungern Sternberg, a Baltic German painter (1773–1830).

caused by the great amount of residue left by platinum separation. The Finance Minister, Count Egor Kankrin (1775–1845), became worried about the possible loss of platinum in the residue and sent samples of native platinum to eminent persons and institutions both at home and abroad. One of the participants in the research was J. J. Berzelius[6] in Sweden, who analysed the raw platinum in the

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[6] Jöns Jacob Berzelius (1779–1848), professor of chemistry at Karolinska Institutet in Stockholm, honorary doctor of Tartu University from 1827. He had high reputation in the whole of Europe and several well-known chemists used the opportunity to work in his laboratory: F. Wöhler, G. Rose, G. Magnus, and others.

In the Ural Mountains osmium–iridium ore was first found in 1819 and at the beginning of the 1820s a very rich deposit of platinum ore was discovered in Nizhni Tagil, central part of the Urals. The centre of the investigation of platinum metals in the Russian Empire was the united laboratory of the Mining Department and the Mining Cadets Corps (later institute) in St. Petersburg. The leading role in these investigations was played by the mining engineers Vassili Lyubarskij (1795–1852) and Petr Sobolevskij (1789–1841), whose method for the separation of platinum from ore was introduced into practice in 1827–1828. This method[9] was used to produce the metal for coins [19].

Analysis of ore from Nizhni-Tagil [17]

Beginning the analysis with 1.305 g of ore Osann used the well-known in Europe scheme by which the platinum metals were dissolved by treatment with a mixture of nitric and hydrochloric acids. The indissoluble residue (0.0235 g) was left aside and the solution was analysed. The course of the analysis is shown in Scheme 1.

The composition of the ore (Fig. 3) received by Osann and calculated in % by H.H. was: 83.06% Pt, 10.80% Fe, 1.92% Ir, 1.30% Cu, 0.59% Rh, 0.27% Pd, and 1.80% indissoluble residue [17]. The loss at analysis was 0.26%. For detailed analysis of indissoluble residue more primary matter was needed. Osann ordered from St. Petersburg a new portion of crude platinum and used 100 g of it for the next course of analysis paying greatest attention to the indissoluble residue.

Analysis of residue indissoluble in acids [17]

After treatment of crude platinum with nitric and hydrochloric acids the indissoluble residue was separated. The residue was treated by potassium hydroxide solution, dried, three crystals of potassium nitrate were added, and then melted. Some water was added to the cooled melt and after the partial dissolution of the melt, nitric acid was added. A black precipitate was formed and the mixture had an unpleasant smell. According to Osann, that smell indicated the presence of osmium in the mixture. The mixture was distilled in a retort to evaporate the gaseous osmium oxide (OsO_4, H.H.). The distillation was interrupted when half of the mixture was left, and the remainder was cooled. After 24 h Osann discovered there long prismatic white slightly pink crystals with a specific lustre. The crystals dissolved when water was added to the distillation residue, but formed again after the residue was warmed and cooled. Osann made three tests with crystals and found that (1) the crystals partly sublimated at heating with blowpipe on charcoal, (2) from the solution in hydrochloric acid a dark grey layer was formed on a zinc stick, (3) the heating test in a glass pipe with both ends fused showed that the

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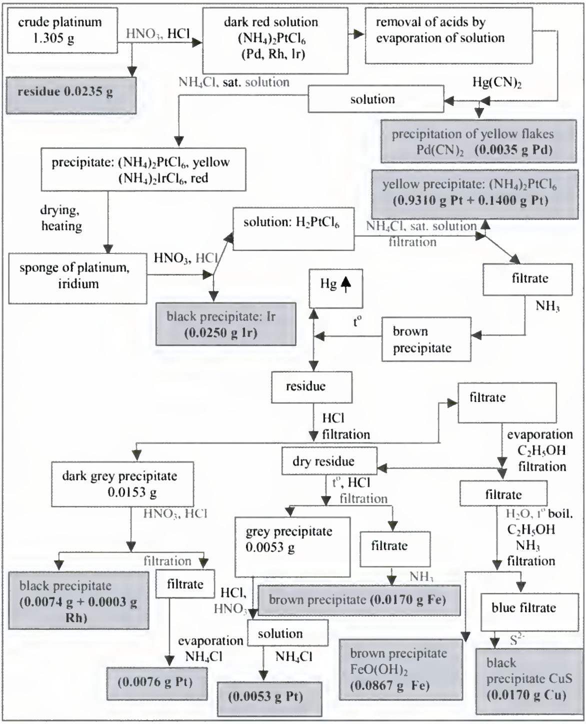
[9] The ore was treated with aqua regia, the indissoluble part was filtered, and platinum was precipitated from the received solution as chlorocomplex of ammonia. By thermal decomposition of the precipitate platinum formed a porous spongy mass. Pressing the sponge yielded a well malleable platinum. The method used in Europe was introduced by Wollaston and was kept secret for a long time but did not differ very much from the Russian method used in St. Petersburg.


crude platinum 1.305 g
HNO3, HCl
dark red solution (NH4)2PtCl6 (Pd, Rh, Ir)
removal of acids by evaporation of solution
residue 0.0235 g
NH4Cl, sat. solution
Hg(CN)2
solution
precipitation of yellow flakes Pd(CN)2 (0.0035 g Pd)
precipitate: (NH4)2PtCl6, yellow (NH4)2IrCl6, red
yellow precipitate: (NH4)2PtCl6 (0.9310 g Pt + 0.1400 g Pt)
drying, heating
solution: H2PtCl6
NH4Cl, sat. solution
filtration
sponge of platinum, iridium
HNO3, HCl
Hg
filtrate
NH3
black precipitate: Ir (0.0250 g Ir)
t°
brown precipitate
residue
filtrate
HCl
filtration
evaporation
C2H5OH
filtration
dry residue
dark grey precipitate 0.0153 g
t°, HCl
filtration
filtrate
HNO3, HCl
grey precipitate 0.0053 g
filtrate
H2O, t° boil.
C2H5OH
NH3
filtration
filtration
NH3
black precipitate (0.0074 g + 0.0003 g Rh)
filtrate
HCl, HNO3
brown precipitate (0.0170 g Fe)
blue filtrate
solution
S2-
evaporation
NH4Cl
NH4Cl
brown precipitate FeO(OH)2 (0.0867 g Fe)
black precipitate CuS (0.0170 g Cu)
(0.0076 g Pt)
(0.0053 g Pt)

Scheme 1. Analysis of the platinum ore from Nizhni-Tagil [17]. (According to the description of the analysis, H.H.)

crystals in the one end of the pipe vaporized (sublimized) fully forming in the other end of the pipe small lustering needles. Osann was convinced that no known substance behaved similarly. He excluded osmium because the substance did not smell and distil as a liquid. It did not resemble oxides of bismuth, tellurium, or antimony either.[10]

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[10] It was later found that ruthenium solution when treated with nitric acid forms by hydrolysis several hydroxocomplexes with a coordinated NO group, which are indissoluble in the region of pH 2–9 [20].

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Osann had used for the analysis 0.1 g of the produced crystals and decided that it would be most reasonable to send the left 0.3 g to Berzelius. In the same paper where Osann describes the analysis [17] he presents also the answer from Berzelius:

> Stockholm d. 10. April 1828. Soviel ich daraus ersehen kann, haben Sie darin einen neuen Stoff gefunden. Denn ich kann aus den kleinen sublimirbaren Krystallen nichts Bekanntes bekommen.[11]

Berzelius had made with the crystals the test with ammonium sulphide and had a precipitate of easily melting grey sulphide turning transparent and yellowish red at heating. At cooling the substance changed again grey and nontransparent. He made also a sublimation test with the crystals.

Repetition of the analysis of residue [17]

After Berzelius had confirmed the presence of an unknown element, Osann ordered again 100 g of the same kind of platinum from St. Petersburg and repeated the analysis applying the same method as earlier. Yet after the treatment with nitric acid only a very small amount of crystals similar to those received in the earlier analysis were found. The amount of crystals was too small to identify them. However, Osann made here an essential conclusion, supposing that if the new substance formed a volatile oxide like osmium did, it could go over into the distillate together with osmium.[12]

The distillate received by Osann smelled like an osmium compound and it turned dark blue at the addition of gallnut tincture. At saturation with sodium chloride an osmium salt of gallic acid[13] precipitated. The precipitate was filtered and ammonium sulphide was added to the filtrate. By that a small amount of grey precipitate formed, which could be a sulphide of a new metal. These tests convinced Osann that a new metal was present. He named the metal ruthenium, obviously in honour of Russia after its medieval Latin name. At the end of his paper [17] he mentioned that there was another element in a larger amount present, and that he intended to name it pluran:

> Dieses Wort ist zusammengesezt aus den Anfangsbuchstaben des Platins und der Urals.[14]

Detailed analysis of platinum residue

In 1828 Osann published also another paper in *Poggendorff's Annalen* [18], where he discussed the analysis of the residue of the treatment of crude platinum by acids in detail. Osann modified only a few details in the preliminary course of analysis. However, the changes made caused essential changes in the results. The description of the whole qualitative analysis is very capacious and it is convenient to follow its course in Scheme 2. In the scheme only the operations that were repeated many times one after another, caused by the occurrence of after-precipitation, are omitted. For clarity the scheme is divided into seven steps.

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[11] Translation: As much as I can understand you have found a new substance and I cannot detect in the little crystals, which are able to sublimate, any familiar [substance].

[12] RuO_4 is volatile but needs for forming a stronger oxydant than OsO_4 does; its boiling point is lower, H.H.

[13] *Gallussaure osmiumoxide* by Osann, H.H.

[14] Translation: That word is put together of the initial letters of platinum and Urals.

Step I. First the platinum residue was mixed with potassium hydroxide and heated in the presence of potassium nitrate as oxidant. The melt was digested by water and the alkaline sample was distilled in the retort until a dry residue formed. (In the first analysis the alkaline solution was acidified before distillation.)

Step II. Great attention was paid to the analysis of the distillate from Step I. Ethyl alcohol was added to the distillate as reductant, and a black precipitate formed. The precipitate was filtered and melted with potassium hydroxide. Nitric acid was added to the melt and the acidified sample was distilled. Osann expected that pink crystals would form in the distillation residue as had happened in his first analysis but could not find them. He concluded that if the new element had formed a volatile compound (as he had stated already earlier) it had gone to the distillate. He made with the distillate the tests known for osmium and had positive results. (Actually ruthenium has very similar reactions: it colours the solution with tannic acid bluish green and reduces with ethyl alcohol as well as with zinc forming a black precipitate. H.H.)

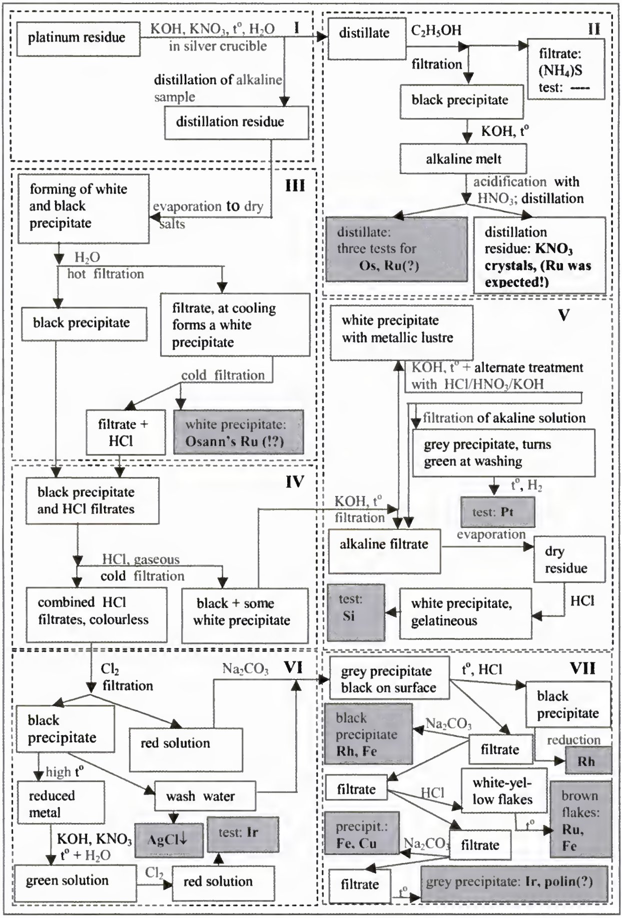
Step III. The alkaline distillation residue was evaporated to dry, and a mixture of white and black precipitate formed. At hot filtration the white precipitate dissolved and the black precipitate remained on the filter. When the filtrate was cooled a white precipitate formed again. Osann was convinced that it was a compound of a new element. Here Osann was mistaken. He made numerous chemical and blow-pipe tests with the white oxide with a grey tint and could not detect any known element. He tried to reduce the oxide to metal and obtained a tiny gold-yellow grain. He wrote [18, p. 339]:

> Da dieses Metall, welches ich nach den so eben beschriebenen Eigenschaften als ein neues glaube annehmen zu müssen, sich in grösserer Menge als das früher erwähnte in dem uralschen Platin befindet, und auch durch seinen schönen, dem Golde ähnlichen metallischen Glanz sich mehr empfiehlt, so glaube ich, das der Vorschlag, das zuerst aufgefundene neue Metall Ruthenium zu nehmen, besser auf dieses angewendet werden können.[15]

In a later paper, published in 1829 [21], he confessed that the white precipitate was mainly silicium oxide, which precipitated from the solution at the repetition of the acid–alkali treatment and he eliminated the presence of a new metal in the white precipitate.

---

[15] Translation: As the metal that by tests seems to be a new element occurs in a bigger amount in platinum from the Ural than the earlier one, and also has a golden metallic lustre, I think that the name ruthenium that was used for the metal found earlier fits better for the element found later.


I
platinum residue
KOH, KNO$_3$, t°, H$_2$O
in silver crucible
distillation of alkaline sample
distillation residue
II
distillate
C$_2$H$_5$OH
filtration
filtrate: (NH$_4$)S test: ----
black precipitate
KOH, t°
alkaline melt
acidification with HNO$_3$; distillation
distillate: three tests for Os, Ru(?)
distillation residue: KNO$_3$ crystals, (Ru was expected!)
III
forming of white and black precipitate
evaporation to dry salts
H$_2$O
hot filtration
black precipitate
filtrate, at cooling forms a white precipitate
cold filtration
filtrate + HCl
white precipitate: Osann's Ru (!?)
IV
black precipitate and HCl filtrates
HCl, gaseous
cold filtration
combined HCl filtrates, colourless
black + some white precipitate
V
white precipitate with metallic lustre
KOH, t° + alternate treatment with HCl/HNO$_3$/KOH
filtration of akaline solution
grey precipitate, turns green at washing
t°, H$_2$
test: Pt
KOH, t°
filtration
alkaline filtrate
evaporation
dry residue
HCl
white precipitate, gelatineous
test: Si
VI
Cl$_2$
filtration
Na$_2$CO$_3$
black precipitate
red solution
high t°
reduced metal
wash water
AgCl↓
test: Ir
KOH, KNO$_3$
t° + H$_2$O
green solution
Cl$_2$
red solution
VII
grey precipitate black on surface
t°, HCl
black precipitate
black precipitate Rh, Fe
Na$_2$CO$_3$
filtrate
reduction
Rh
filtrate
HCl
white-yellow flakes
t°
brown flakes: Ru, Fe
precipit.: Fe, Cu
Na$_2$CO$_3$
filtrate
filtrate
t°
grey precipitate: Ir, polin(?)

Scheme 2. Detailed qualitative analysis of platinum residue (indissoluble in acids) [18]. (According to the description of the analysis, H.H.)

Step IV. The black precipitate received in Step III was added to the combined hydrochloric filtrates and the mixture was saturated with gaseous hydrochloride. The black precipitate was now separated by filtration.

Step V. The black precipitate was treated alternately with alkali and acids and finally platinum and silicious oxide were detected.

Steps VI and VII. In combined hydrochloric filtrates Osann detected several metals: Ir, Fe, Cu, Rh, Fe–Rh, Fe–Ru, and Ir or a questionable new element polin. Prof. Carl Claus[16], who analysed the platinum ores about 20 years later in Kazan University, Russia [22], was of the opinion that Osann could not have discovered ruthenium because he had not examined the hydrochloric filtrates carefully enough. In his latest paper about platinum analysis Osann refuted Claus's accusation referring to steps VI and VII of the scheme. He wrote in his paper in *Poggendorff's Annalen* 1845 [23]:

> Wenn der Hr. Prof. Claus angiebt, es sey mir die Entdeckung des Rutheniums entgangen, weil ich die salzsauren Auszüge des weissen Oxyds nicht untersucht hätte, so irrt er sich. In meiner Abhandlung über den Platinrückstand, welche in den Annalen von Poggendorff, Bd. 14 (1828) abgedruckt ist, wird er die Untersuchung der salzsauren Auszügen S. 349 bis 352 finden.[17]

In step VI gaseous chlorine as oxidant was passed through the combined hydrochloric filtrates. As a result, the solution coloured red, and a black precipitate formed. In that precipitate iridium was found. In the washing water of the precipitate whitish yellow silver chloride fell down and was filtered. Silver evidently came from the silver crucible used for melting the sample with potassium hydroxide and nitrate. After the filtration of the silver chloride the hydrochloric filtrates were alkalized with soda. After some days (Step VII) a grey precipitate with a black surface appeared. The precipitate was dried and digested with hydrochloric acid. A small amount of a black powder was left, filtered, and reduced to metal, which was evidently rhodium.

The hydrochloric filtrate was alkalized with soda. A black precipitate, which evidently belonged to rhodium and iron, formed. The alkaline filtrate was acidified with hydrochloric acid. In the solution whitish yellow flakes formed. The precipitate was filtered and dried. The dry residue had a reddish brown colour and was identified as a compound of ruthenium and iron. The acidic filtrate was neutralized with soda and a brownish grey precipitate of iron and copper compounds was formed. To identify the precipitate it was filtered and dissolved in hydrochloric acid. Ammonia was added to the solution, and iron precipitated as oxihydroxide. Copper stayed in the solution forming a blue complex with ammonia. The alkaline filtrate received by filtration of iron and copper compounds was evaporated to dry. A grey residue that reminded sponged platinum formed. Osann made eleven different tests but did not get a clear enough answer about the character of the grey powder. Osann declared:

---

[16] Carl Claus (1796–1864) was born in Tartu to a Baltic German family. He was educated and started to work at Tartu University. He worked also at Kazan University and later until his death again at Tartu University.

[17] Translation: If Mr. Prof. Claus refers that I have missed the discovery of ruthenium as I have not investigated the hydrochloric extract of the white oxyde, he deceives himself. In my treatment of the platinum residue, printed in *Poggendorff's Annalen*, Vol. 14 (1828), he can find the investigation of hydrochloric extract from p. 349 to p. 352.

> Obwohl nun dieses Metall sich durch seine Auflöslichkeit in Säuren, so wie durch die Eigenschaft, keinen orangefarbenen Platinsalmiak zu geben, wesentlich vom Iridium unterscheidet[18] so bin ich doch der Meinung, berücksichtigend das Mangelhaft unserer Kenntnisse der Eigenschaften des Iridiums, mit dem Ausspruch der Neuheite dieses Metall, zurückhalten, bis unsere Kenntnisse über diesen Gegenstand eine grössere Erweiterung werden erlangt haben. Sollte sich der aufgefundene Unterschied bewähren, so schlage ich den Name Polin vor (von πολιοζ grau). Bis dahin nehme ich es einstweilen als Iridium an. [18][19]

Osann could now summarize the elemental composition of the platinum residue as follows: osmium, ruthenium, silica, iridium, iron, platinum, copper, and traces of rhodium. He calculated an approximate quantitative relationship of the constituents: osmium, ruthenium, and iridium each made up 25% and the remaining 25% consisted of the other elements.

Complementary analysis of the part of platinum ore dissoluble in acids

Osann made a complementary analysis [18] for the part of platinum ore dissoluble in nitric and hydrochloric acids mainly to check the content of rhodium. After the evaporation of the excessive acid in solution, palladium dicyanide was precipitated. The difference from the earlier analysis [17] was that the filtrate was saturated with soda instead of ammonium chloride (Scheme 1). At saturation a dark brown precipitate was formed. The sublimation test of the precipitate in a glass tube gave two sublimates. The one formed first was taken from the glass tube together with the residue of soda and sublimized again in another glass tube. That sublimate proved to be mercury. The second sublimate (0.0012 g) was dissolved in hydrochloric acid. The solution was saturated with ammonia, and when sulphide ammonia was added a greyish brown precipitate formed. Based on these two properties – sublimation and formation of an insoluble sulphide – Osann concluded that he had here the "new" element mentioned already earlier and named pluran.

The final results of the analysis of platinum ore received by Osann were: the part soluble in acids: Pt 80.87%, Fe 10.92%, Rh 4.44%, Cu 2.30%, Pd 1.301%, pluran 0.06%, and traces of S, Ti, and Os; the insoluble part (0.113%): Os, Ru, and Ir 0.081%; silica, Fe, Pt, Cu, and traces of Rh 0.027% (the missing 0.005% is evidently a mistake caused by the rounding of numbers, H.H.) [18].

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[18] Osann used a test where in the presence of iridium the nitric and hydrochloric acid solution of platinum coloured orange when ammonium chloride was added. H.H.

[19] Translation: Although this metal substantially differs from iridium by its solubility in acids as well as by the property not to form any orange-coloured compound of platinum and ammonia[18] I am still of the opinion that looking back at our deficient knowledge about the properties of iridium, we must restrain from declaring the novelty of that metal until our knowledge in that field extends. But, if the determined differences are valid, I propose the name polin (*πολιοζ*, *grey*). Until then I will regard it temporarily as iridium.

G. W. OSANN LEAVES TARTU AND SETTLES IN WÜRZBURG

Looking back at the years Osann spent in Tartu it seems that he was there unwillingly, waiting for an opportunity to return to Germany. His letter to J. B. Trommsdorff[20] in 1825 [24] reveals that Osann planned to establish in Germany a factory to produce tartaric acid and potassium hydroxide from the potassium tartrate forming in the wine industry. He wrote that he had no expectations for a sufficient heritage and so he hoped that that idea could provide a source of an additional income in the future and asked for advice. His project was never realized as we know and his career remained academic.

In 1828 Osann was invited to Würzburg University to become professor of physics and chemistry. In his letter of 12 March 1828 to the Council of Tartu University he asked to relieve him of his post at the University in connection with his moving to Würzburg [26]. The same day Osann wrote to the apothecary Burchard in Reval[21] that he was leaving Estonia and asked him to give his best greetings to his friends in Reval:

> Meinen Freunden in Reval, gibt es andere dergleichen... Reval mit seinen schicken Umgäbungen werde ich daher nicht wieder sehen. [27][22]

Osann had a good reputation as a productive writer of textbooks and he was known, with some reservations, as the discoverer of a new platinum element – ruthenium. Some confusion about that fact was caused by his hurriedly made announcement of the discovery of two other elements – pluran and polin. In 1829 he answered in *Poggendorff's Annalen* [21] to the letter published by Prof. Berzelius, who was suspicious about the occurrence of a new element in the white oxide received by Osann in the analysis of the platinum residue. Osann agreed with Berzelius that the white oxide he received in the analysis of platinum residue was really a combined precipitate of titanium acid, zirconium oxide, and silica and not a new element. In 1841–1842 Prof. Carl Claus at Kazan University in Russia began to research the platinum metals and after successful separation of pure ruthenium in 1844 identified its properties. Claus was everywhere noted as the discoverer of ruthenium. However, he used the name given by Osann – ruthenium. Osann wrote in his paper in 1845 [23] that it was excellent for science if the same discovery had proof by two scientists. Osann himself repeated in

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[20] Johann Bartholomäus Trommsdorff (1770–1837) is founder of scientific pharmacy. He published a critical review about Osann's book *Beiträge zur Chemie und Physik* [4] in the *Taschen-Buch für Chemiker und Apotheker* [25] in 1825. He approved Osann's text-book and said that he was a sharp-sighted naturalist and a good experimentator.

[21] Now Tallinn, the capital of Estonia.

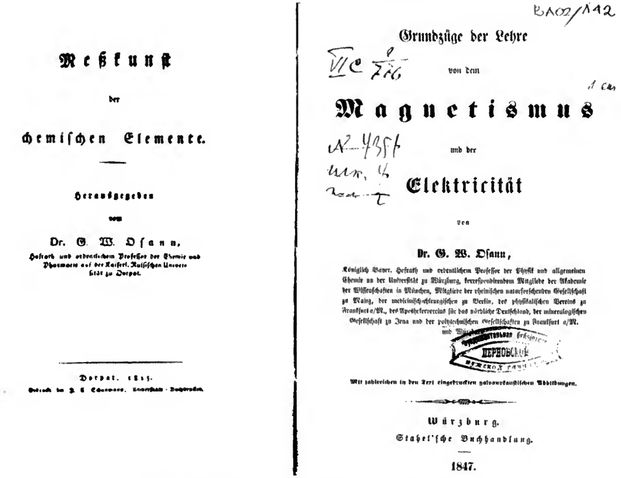
[22] Translation: My friends in Reval, does anywhere exist any similar… Reval with its marvellous surroundings that I can never see again.

Würzburg the analysis of platinum residue received from St. Petersburg, but received nothing new.

Osann began an effective work in educational and scientific fields. His attention was attracted increasingly more by problems of physics such as electrical phenomena, electromagnetism, electroinduction, and light phenomena. He published nearly 50 papers (see for examples Fig. 4), mostly in K. W. G. Kastner's journal *Archiv für die gesammte Naturlehre* and O. L. Erdmann's *Journal für technische und ökonomische Chemie* [28, 29].

Some papers from the Würzburg period [30] are given as examples:

1843–1846	"Neue Beiträge zur Chemie und Physik"
1836	"Analyse des Mineralwassers vom Ludwigs-Brunnen zu Gross-Karben in der Wetterau... in Oberhessen"
1847	"Grundzüge der Lehre von dem Magnetismus und der Elektricität" (Fig. 4)
1849	"Programm über die Bedeutung der Naturlehre unter den allgemeinen Wissenschaften"
1849	"Darlegung mehrere neuer Versuche über Gassäulen und das Ozon"
1852	"Erfahrungen in dem Gebiete des Galvanismus gesammelt. Für Physiker, Chemiker und Techniker"



Meßkunſt
der
chemiſchen Elemente.

Herausgegeben
von
Dr. G. W. Oſann,
Hofrath und ordentlichem Profeſſor der Chemie und
Pharmacie auf der Kaiſerl. Ruſſiſchen Univerſität zu Dorpat.

Dorpat, 18[illegible].
[illegible]

BA02/142

Grundzüge der Lehre
VIIc 7/76
von dem
1 cm
Magnetismus
N 4357
und der
ukr. 4
Elektricität

von

Dr. G. W. Oſann,
Königlich Bayer. Hofrath und ordentlichem Profeſſor der Phyſik und allgemeinen Chemie an der Univerſität zu Würzburg, correſpondirendem Mitgliede der Akademie der Wiſſenſchaften in München, Mitgliede der rheiniſchen naturforſchenden Geſellſchaft zu Mainz, der mediciniſch-chirurgiſchen zu Berlin, des phyſikaliſchen Vereins zu Frankfurt a/M., des Apothekervereins für das nördliche Deutſchland, der mineralogiſchen Geſellſchaft zu Jena und der polytechniſchen Geſellſchaften zu Frankfurt a/M. und Wür[illegible]

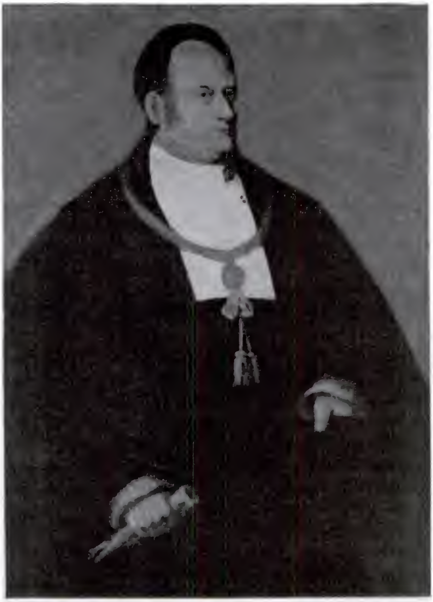
ПЕРНОВСКОЙ

Mit zahlreichen in den Text eingedruckten galvanokauſtiſchen Abbildungen.

Würzburg.
Stahel'ſche Buchhandlung.

1847.

Fig. 4. Examples of publications by G. W. Osann.



Gottfried Wilhelm Osann

Fig. 5. Rector of Würzburg University Dr. G. W. Osann. From: Koschel, K. & Sauer, G. *Zur geschichte des Chemischen Instituts der Universität Würzburg*, 1968; original in the Institute of Pharmacy of Würzburg University. The oil painting is not signed, but the probable name of the painter and date are found on its back side: J. Hahn, 1863. The author is grateful to the colleagues from Würzburg University, chair of pharmaceutical technology, who discovered that fact.

Osann took actively part in the academic life. He belonged as a foundation member to the society Physikalisch-medizinischen Gesellschaft zu Würzburg, was Royal Bavarian privy councillor, corresponding member of Munich Academy of Science, and member of many other societies. In 1840/41 Osann was elected dean and in 1848/49, rector of Würzburg University (Fig. 5). The subject of his promotion speech was the significance of the natural studies among the sciences. He said:

> Die Kunst Beobachtungen zu verstehen, macht den Naturforscher. Es gehört Kenntnis und Urtheil dazu, in einer Beobachtung das heraus zu finden[!], was bekannt und was neu ist. Mitunter waren es ganz geringfügige von Vielen übersehene *Umstände*, welche zu den grössten Entdeckungen geführt haben. [31][23]

The last paper by Osann was published in the journal *Würzburger Naturwissenschaftliche Zeitschrift* in 1866. It was about the thunderclap into the tower of a church in Würzburg on 6 January 1865 [32].

Gottfried Wilhelm Osann died in Würzburg on 10 August 1866 [1, 8].

DISCUSSION

The question about the priority of the discovery of ruthenium can be answered only on the ground of a thorough study of the analysis and conclusions made by Osann using the modern knowledge about the chemistry of ruthenium.

Following Osann's analysis we must agree that the properties of the new element described by him belong to ruthenium: mineral acids do not affect the metal and it is dissolved by alkaline oxidizing fusion (Scheme 2, Step I). As a result ruthenium forms soluble ruthenate (VII, VI)-ions, staying in distillation residue (Step III) and/or forms volatile ruthenium (VIII) tetroxide RuO_4, which is detected in the distillate (Step II). Tetroxide is usually reduced by hydroxide ion and it forms ruthenate ions. It is easily reduced also by ethyl alcohol forming oxides such as black ruthenium sesquioxide Ru_2O_3 or brownish black dioxide RuO_2. Hydrous oxides are commonly precipitated in alkaline solution. When freshly precipitated, they may be soluble in acids, but after aging only with great difficulty or not at all (Steps IV–VII) [33].

It must also be taken into consideration that Carl Claus left the name of the element given by Osann – ruthenium – unchanged. Thus he indirectly recognized the rights of Osann to the discovery.

We must remember that after analysing the pink crystals received by Osann Berzelius declared that nothing already known could be found and consequently the crystals had to belong to a new element.

The trouble of Osann was that he could not repeat his results and was not sure in his conclusions. As Berzelius said – he involved himself in details. The "discovery" of two other elements, polin and pluran, caused misunderstanding and overshadowed the discovery of ruthenium. Osann had serious difficulties to analyse the too small quantities of samples for the determination of the element accounting for 1–2%. It was not always possible to make enough tests with the received compounds.

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[23] Translation: The art to understand the observations will make the naturalist. For that we need the knowledge and ability to distinguish between what is new and what is already known. Sometimes there are absolutely insignificant details among the facts of the case that will lead to the great discovery.

Claus analysed platinum residue 16 years later. He had at his disposal enough substance and the experiences of Osann. Prof. Carl Claus had worked in the same laboratory where Osann had worked earlier. Claus has the honour of isolating ruthenium as a pure element and determining the properties of the new element.

Concluding finally all the for and against arguments we can attribute the priority of the discovery of ruthenium to G. W. Osann.

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Gottfried Wilhelm Osann ja ruteenium

Helvi Hödrejärv

Gottfried Wilhelm Osann (1797, Weimar–1866, Würzburg) oli Tartu ülikooli (*Universitas Dorpatensis*) keemiaprofessor aastatel 1823–1828. Sel perioodil analüüsis ta Uurali mäestikust pärit toorplaatinat, avastas uue plaatinametalli ja nimetas selle Venemaa ladinakeelse nime järgi ruteeniumiks. Kuna Osann sai uut elementi väheses koguses, ei õnnestunud tal seda metallina isoleerida. Selle saavutas mitmeid aastaid hiljem ja avaldas 1844. aastal Venemaal Kaasanis tegutsev Carl Claus, säilitades Osanni poolt antud nimetuse. Carl Clausi nimetatakse sageli ruteeniumi avastajaks, unustades märkida G. W. Osanni osa.

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В	в	v	К	к	k	Т	т	t	Ъ	ъ	
Г	г	g	Л	л	l	У	у	u	Ы	ы	y
Д	д	d	М	м	m	Ф	ф	f	Ь	ь	
Е(Ё)	е(ё)	e	Н	н	n	Х	х	kh	Э	э	é
Ж	ж	zh	О	о	o	Ц	ц	ts	Ю	ю	yu
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